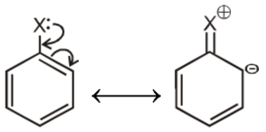
Exercise-1

Marked Questions may have for Revision Questions.

PART - I : OBJECTIVE QUESTIONS

Section (A) : Unimolecular Nucleophilic substitution reactions of alkyl halides (S_N1)

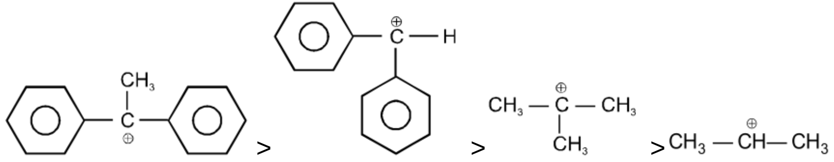
A-3. **Sol.** In aryl halides the C–X bond has partial double bond character due to resonance so the cleavage of
C–X bond becomes difficult.



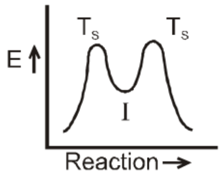
A-5. **Sol.** S_N1 reactions occur through the intermediate formation of carbocations.

A-6. **Sol.** S_N1 reactions are favoured by bulky groups on the carbon atom attached to the halogen atom.

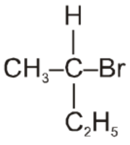
A-9. **Sol.** Rate of $S_N1 \propto$ stability of C^+.



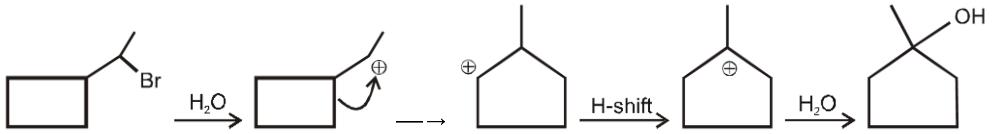
A-10. **Sol.**



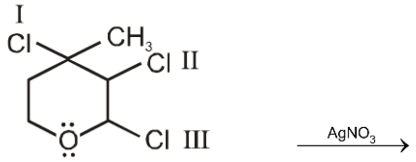
A-12.

Sol.  $CH_3-\overset{\overset{\large H}{|}}{\underset{\underset{\large C_2H_5}{|}}{C}}-Br$ give racemic mixture in S_N1 reaction because it has chiral carbon.

A-14. **Sol.**



A-15. **Sol.**



S_N1 Reaction

Reaction Intermediate — Carbocation :

III will give most stable carbocation ⇒ stabilised by +m effect of $-\ddot{\underset{\cdot\cdot}{O}}-$

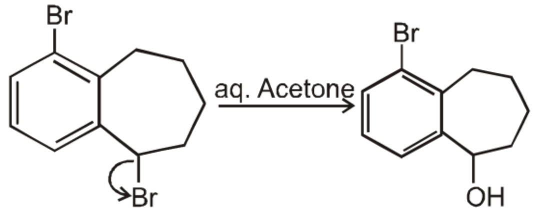
I will give stable carbocation $\longrightarrow$ 3º carbocation so order of reaction = III > I > II.

A-17. **Sol.** $(C_6H_5)_3CCl$ give most stable carbocation.

A-18. **Sol.** Rate of hydrolysis $\propto$ stability of formed carbocation intermediate

A-19. **Sol.** The given reaction is hydrolysis and it follows SN^1 mechanism and both I and II are formed.

A-20. **Sol.**



In aryl halides the C–X bond has partial double bond character due to resonance so it will not give S_N1 reaction.

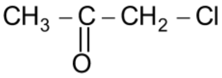
Section (B) : Biomolecular Nucleophilic substitution reactions of alkyl halides (S_N2)

B-4. **Sol.** S_N2 mechanism is single step concerted process and transition state is fromed.

B-5. **Sol.** 1, 2 and 4 are highly crowded molecules so they do not give S_N2 reaction.

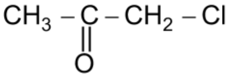
B-6. **Sol.** S_N2 reaction involves transition state, there is no intermediate.

B-7. **Sol.**


$CH_3-\underset{\underset{O}{||}}{C}-CH_2-Cl$

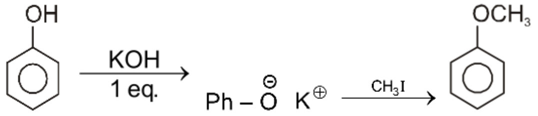
is most reactive due to –I effect of C=O group.

Sol.


$CH_3-\underset{\underset{O}{||}}{C}-CH_2-Cl$

, C=O

B-8. **Sol.**



B-10. **Sol.** $R-X + KCN \xrightarrow{\text{alcohol}} R-C\equiv N$

B-14. **Sol.** $C_2H_5Br + C_2H_5ONa$ $C_2H_5OC_2H_5$

B-15. **Sol.** $\underset{(A)}{C_2H_5Cl} \xrightarrow{NH_3} \underset{(B)}{C_2H_5NH_2} \xrightarrow{C_2H_5Cl} \underset{(C)}{(C_2H_5)_2NH} \xrightarrow{C_2H_5Cl} (C_2H_5)_3N$

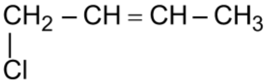
B-16. **Sol.** Acid chloride is more electrophilic than alkyl halide, hence more reactive.

B-18. **Sol.** $CH_3-C\equiv CH \xrightarrow{Na} CH_3-C\equiv C^-Na^+ \xrightarrow{CH_3-CH_2-I} CH_3-C\equiv C-CH_2-CH_3$

B-20. **Sol.** $(CH_3)_2CH-CH_2-CH_2-CH(CH_3)_2$ syntheized in good yield in wurtz reaction

B-21. **Sol.** All reaction are correct

B-23. **Sol.** Order of reactivity towards S_N2 : 1º > 2º > 3º


$\underset{\underset{Cl}{|}}{CH_2}-CH=CH-CH_3$

Section (C) : Nucleophilic substitution (S_N) reaction of alcohols

C-2. **Sol.** Anhy. $ZnCl_2$ and conc. HCl is called Lucas reagent. It is used to distinguish the primary, secondary and tertiary alcohol.

C-4. **Sol.** IV give most stable carbocation while I form least stable carbocation.

C-8. **Sol.** It is S_N1 reaction so racemisation occurs,

C-10. **Sol.**

$$C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl + POCl_3 + HCl$$

$$C_2H_5Cl + AgNO_2 \longrightarrow C_2H_5NO_2 + AgCl$$

C-11. **Sol.** Thionyl chloride method is preferred over phosphorous pentachloride method for the preparation of alkyl chloride because, the by products being gases escape into the atmosphere leaving behind almost pure alkyl chloride.

C-12. **Sol.** It is S_Ni mech so retention of configuration take place in the product.

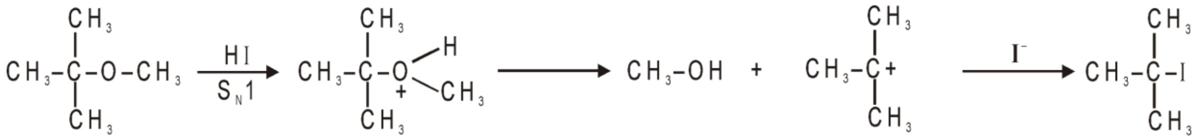
C-13. **Sol.** It is S_N2 mech so inversion of configuration take place in the product

C-14. Sol. It is S_N2 reaction so inversion takes place.

C-15. **Sol.** It is S_Ni reaction so retention takes place

Section (D): Preparation and chemical reactions of ethers

D-1. **Sol.**



D-3. **Sol.** $CH_3 - O - CH(CH_3)_2 + HI \xrightarrow{373\,K} H_3Cl + (CH_3)_2\,CHOH$

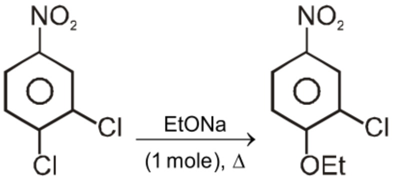
D-5. **Sol.** S_N2 reaction readily occurs on less sterically hindered substrate.

Section (E) : Preparation and nucleophilic substitution of aryl halides

E-1. **Sol.** Because rate of S_N2 Ar is (–F > –Cl > –Br > –I) and –M groups at o/p- positions also increases rate of S_N2 Ar.

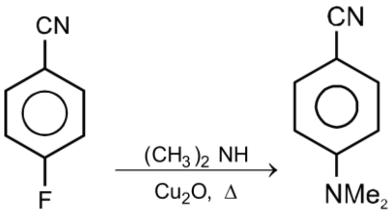
E-2. **Sol.** It is S_N2 Ar reaction. F^{Θ} is L.G., CH_3O^{Θ} is nucleophile.

E-3. **Sol.**

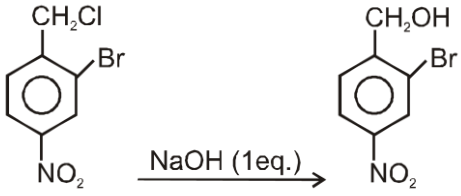


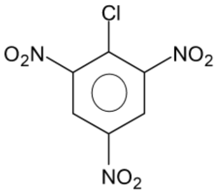
[– M of $–NO_2$ at para position]

E-4. **Sol.**



(S_N2 Ar)

E-5. **Sol.** 

E-7. **Sol.** 

2,4-6 trinitrochlorobenzene has three strong electron withdrawing groups at o/p position which make it highly reactive.

Exercise-2

PART - I : OBJECTIVE QUESTIONS

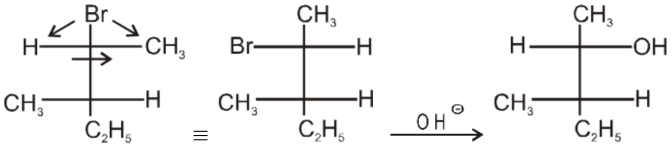
Marked Questions may have for Revision Questions.

5. **Sol.** S_N1 reaction proceed through the formation of carbocation intermediate, which is most favored in more polar solvent.

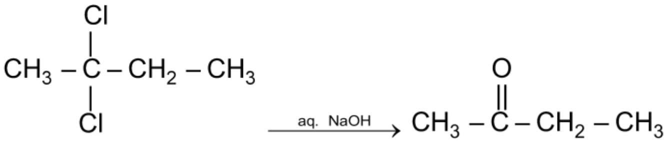
7. **Sol.** Rate of solvolysis $\propto$ stability of carbocation

12. **Sol.** The relative stability of alkyl carbocation is due to inductive effect and hyperconjugation, while that of stable carbocation is due to resonance. The order is :

$CH_3CH_2X < (CH_3)_2CH - X < CH_2 = CH - CH_2X < PhCH_2 - X$.

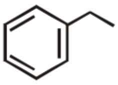
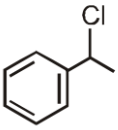
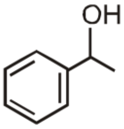
18. **Sol.** 

19. **Sol.** It is S_N2 reaction.

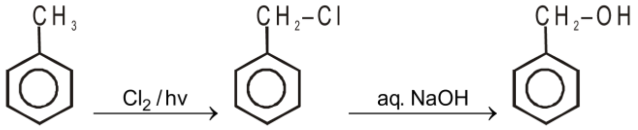
20. **Sol.** 

21. **Sol.** In S_N2 reaction the nucleophile always attack from back side therefore a single stereoisomer is formed with inverted configuration.

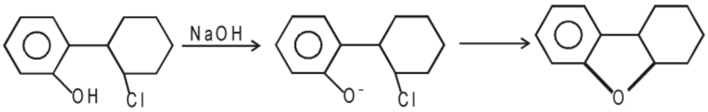
22. **Sol.** Inversion takes place in S_N2 reaction while configuration of nucleophile remains same.

23. **Sol.** A =  B =  C = 

24. **Sol.**



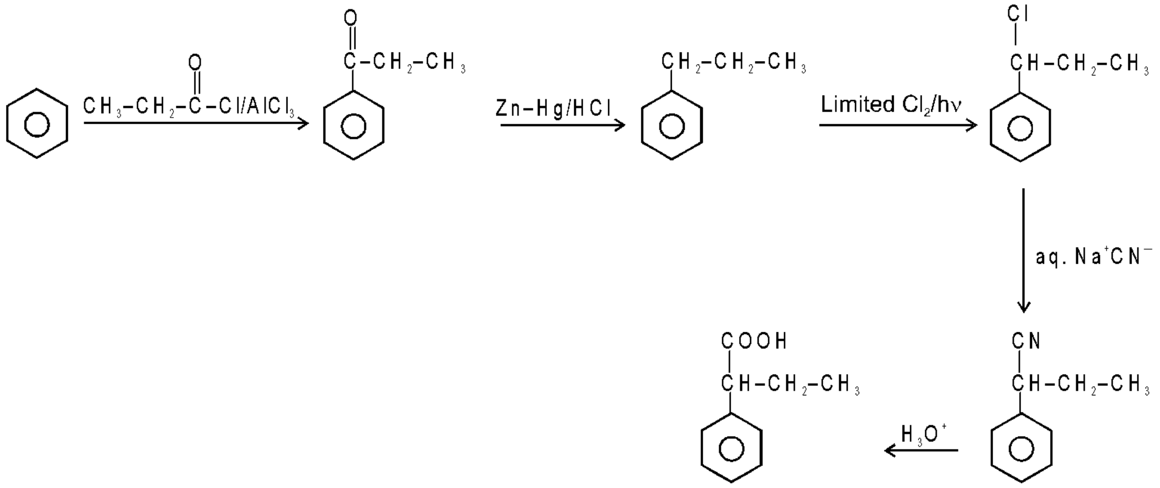
26. **Sol.** Intramolecular S_N2 reaction



28. **Sol.** It is S_N2 reaction

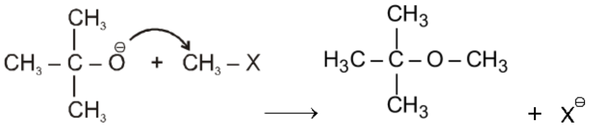
$CH_3-CH_2-Cl + KCN \longrightarrow CH_3-CH_2-CN$
(Propanenitrile)

29.



Sol.

30. **Sol.** Williansons' synthesis : S_N2 reaction
Order of reactivity of alkyl halides : 1º > 2º > 3º

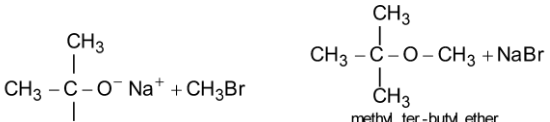


$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\overset{\ominus}{O} + CH_3-X \longrightarrow H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O-CH_3 + X^{\ominus}$$

31. **Sol.** **For synthesis of symmetrical ethers**

$CH_3O^-Na^+ + BrCH_3 \longrightarrow CH_3OCH_3 + NaBr$
dimethyl ether
(symmetrical ether)

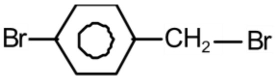
For synthesis of asymmetrical ethers



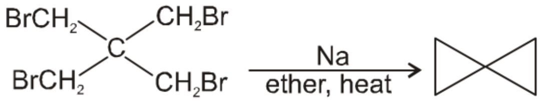
$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O^- Na^+ + CH_3Br \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O-CH_3 + NaBr$$

methyl ter-butyl ether
(asymmetri cal ether)

32. **Sol.** Given reaction in S_N2



34. **Sol.**



38. **Sol.** In Lucas test of alcohols, the appearance of cloudiness is due to the formation of alkyl chlorides

39. **Sol.** The –OH group of alcohol or the –COOH group of a carboxylic acid is replaced by Cl using phosphorus penta chloride (i.e., PCl_5)

$$\underset{\text{Alcohol}}{ROH} + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

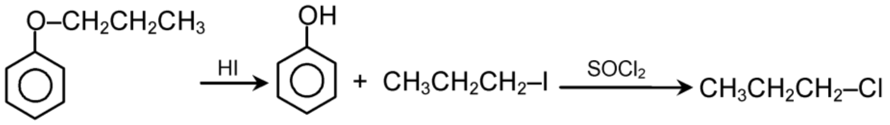
$$\underset{\text{Acid}}{RCOOH} + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

40. Sol. It is S_Ni reaction so retension takes place.

41. **Sol.** In the reaction
ROR' + HX ROH + R'X
the correct order of reactivity of halogen acids is :
HI > HBr > HCl

42. **Sol.** $Et–O–Ph \xrightarrow{HI} Ph–OH + Et–I \xrightarrow{SOCl_2} EtCl.$

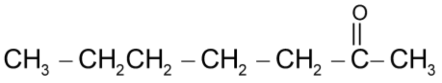
43. **Sol.**



Phenol do not react with thionyl chloride.

44. **Sol.** First reaction is S_N1 reaction because C_2H_5OH used as solvent which is a weak nucleophile.
Second reaction is S_N2 reaction because $C_2H_5O^-$ is strong nucleophile.

47. **Sol.** $CH \equiv CH \xrightarrow{NaNH_2} CH \equiv C^-Na^+ \xrightarrow{C_5H_{11}Br} CH_3CH_2CH_2CH_2CH_2C{\equiv}CH \xrightarrow[H_2SO_4]{Hg^{2+}, H_2O}$



$$CH_3-CH_2CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$$ (Heptan-2-onegsIVsu-2-vkWu)

PART - II : MISCELLANEOUS QUESTIONS

Section (A) : ASSERTION/REASONING

A-1. **Ans.** (1)

A-2. **Ans.** (1)

A-3. **Ans.** (1)

A-5. **Sol.** (1)

A-6. **Ans.** (1)

A-7. **Ans.** (1)
Sol. Intermediate formed during S_N1 is carbocation.

A-8. **Ans.** (4)

A-9. **Ans.** (1)

A-0. **Ans.** (1*)

A-2. **Sol.** (4)
Asseration is false, because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon– chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles.

Section (B) : MATCH THE COLUMN

B-1. **Sol.** Rate of solvolysis ∝ stability of intermediate carbcation.

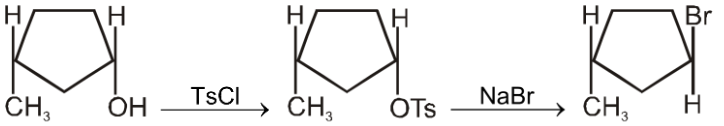
Section (C) : ONE OR MORE THAN ONE OPTIONS CORRECT

C-1. **Sol.** Rate of solvolysis ∝ Stability of carbocation.

C-2. **Sol.** $k_1' < K_1$ ⇐ due to steric hinderence of nucleophile
$k_2' < K_2$ ⇐ due to steric hinderence of nucleophile
$k_1 > K_2$ ⇐ due to steric hinderence of R – X
$k_1' > k_2'$ ⇐ due to steric hinderence of R – X

C-3.

Sol.



Exercise-3

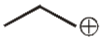
Marked Questions may have for Revision Questions.

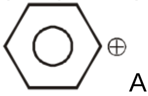
PART - I : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

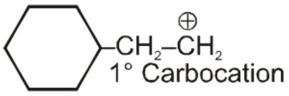
OFFLINE JEE-MAIN

1. **Sol.** S_N1 unimolecular nucleophilic substitution reation is favoured with stability of carbocation.

(1) $(CH_3)_3C^{\oplus}$ (3° Carbocation)

(2)  1° Carbocation

(3)  Aryl Carbocation

(4) 

2. **Sol.** 3° Alkyl Halide give S_N1 reaction with H_2O.

4. **Sol.** Steric hinderance.

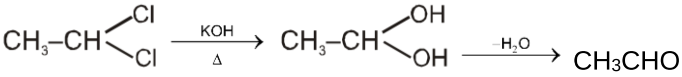
5. **Sol.** In Corey house synthesis of alkane, alkyl halide reacts with lithium dialkyl cuprate.

$R_2CULi + R'X \rightarrow RR' + RCu + LiX$

6. **Sol.** In aryl halides the C–X bond has partial double bond character due to resonance so it will not give S_N reaction

7. **Sol.** The reactivity of a compound towards S_N2 reaction decreases as the crowding at the C-atom containing leaving group increases.

8. **Sol.** CH_3Cl show complete stereochemical inversion during an S_N2 reaction.

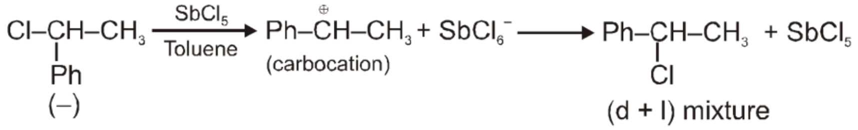
9. **Sol.** 

$CH_3{-}CH\begin{smallmatrix}Cl\\Cl\end{smallmatrix} \xrightarrow[\Delta]{KOH} CH_3{-}CH\begin{smallmatrix}OH\\OH\end{smallmatrix} \xrightarrow{-H_2O} CH_3CHO$

10. **Sol.** Reaction of alcohol with HCl and anhydrous $ZnCl_2$ is an S_N reaction.
3° alcohol react faster with HCl and anhydrous $ZnCl_2$ since it forms more stable carbocation intermediate.

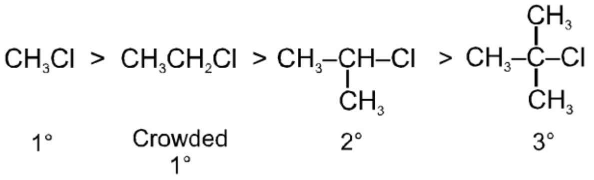
11. **Sol.** Rate of S_N1 reaction stability of carbocation

12. **Sol.**



13. **Sol.** The reaction of alcohol with lucas reagent is mostly an S_N1 reaction and the rate of reaction is directly proportional to the carbocation stability formed in the reaction, since 3° R–OH forms 3° carbocation hence it will react fastest.

14. **Sol.** Rate of S_N2 $\propto \dfrac{1}{\text{Steric crowding of } \alpha \text{ 'C'}}$



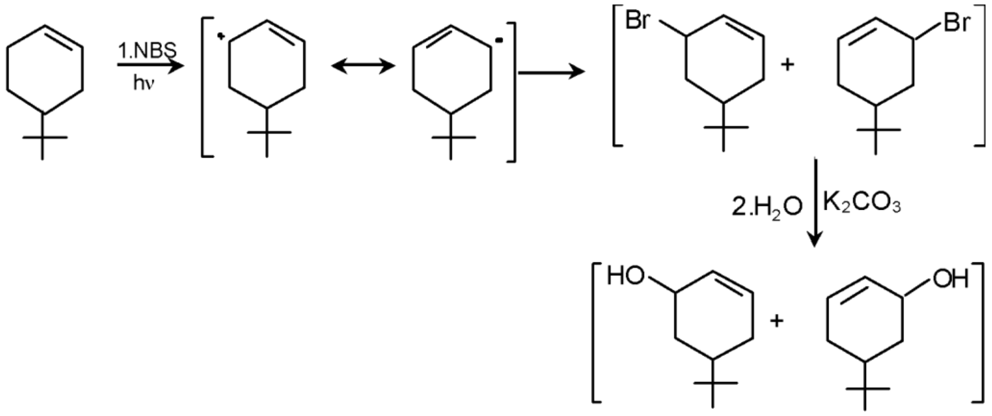
$CH_3Cl > CH_3CH_2Cl > CH_3-\underset{CH_3}{CH}-Cl > CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl$

1° Crowded 1° 2° 3°

15. **Sol.** R–X + AgF $\longrightarrow$ R–F + AgX (Swarts reaction) (LokVZl vfHkfØ;k)

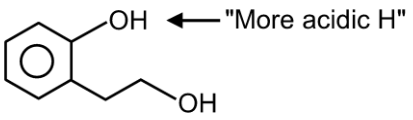
16.

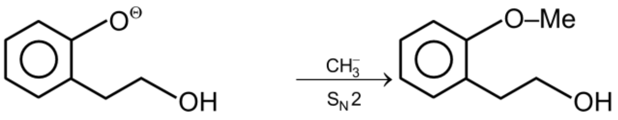
Sol.



ONLINE JEE-MAIN

5. **Sol.**





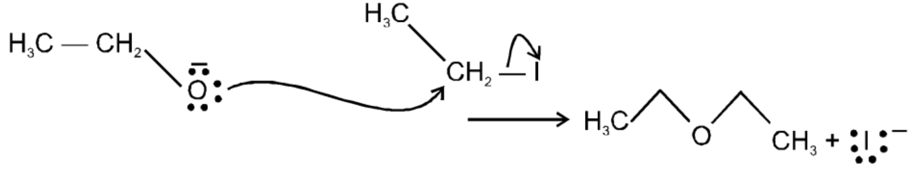
PART - II : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

*** Marked questions may have more than one correct option.**

1. **Sol.** In S_N2 reaction the nucleophile always attack from back side therefore a single stereoisomer is formed with inverted configuration.

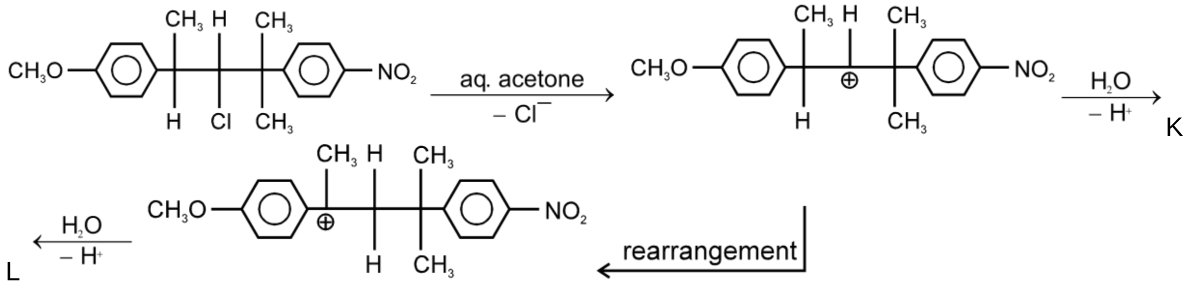
2. **Sol.** Carbon-sulphur bond is weaker than carbon-nitrogen bond. So the -$(CH_3)_2S^+$ is a better leaving group. Therefore react most readily with NaOH to form methanol.

3. **Sol.** It is a S_N2 reaction.
$C_2H_5O^-$ attract the proton from phenol converting the later into phenoxide ion. This would then make nucleophilic attack on the methylene carbon of alkyl iodide, but $C_2H_5O^-$ is in excess $C_2H_5O^-$ is better nucleophile than $C_6H_5O^-$ (phenoxide) ion since while in the former the negative charge is localised over oxygen and in the later it is delocalised over the whole molecular frame work. So, $C_2H_5O^-$ ion make nucleophilic attack at ethyl iodide to give diethyl ether (Williamson's Synthesis).

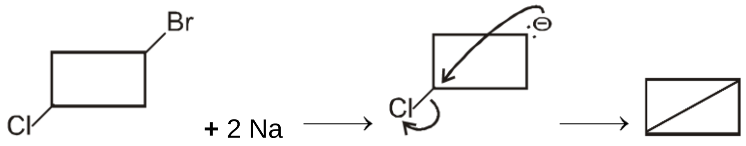


4.

Sol.

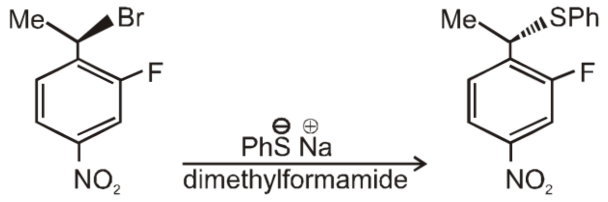


5. **Sol.**

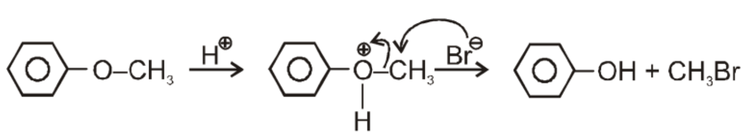


6.

Sol.



It is S_N2 reaction so back side attack is possible.



7. **Sol.**

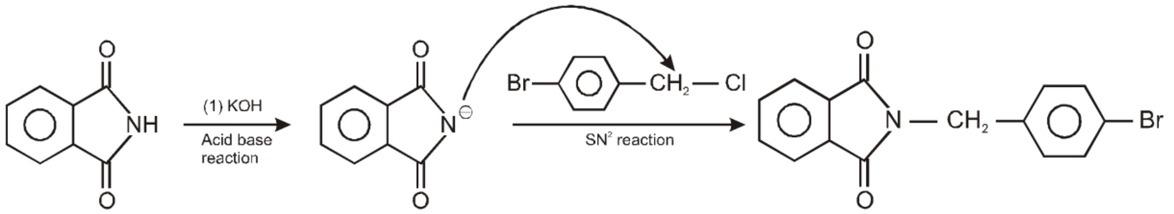
8.

Sol. $CH_3–CH_2–C\equiv C–H \xrightarrow{NaNH_2} CH_3–CH_2–C\equiv C^{\ominus} \xrightarrow{CH_3-CH_2-CH_2-CH_2-Br} CH_3–CH_2–C\equiv C–CH_2–CH_2–CH_2–CH_3$

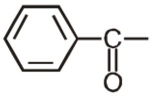
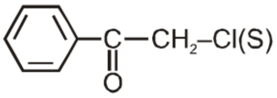
3-octyne (3-vkWDVkbZu)

9.

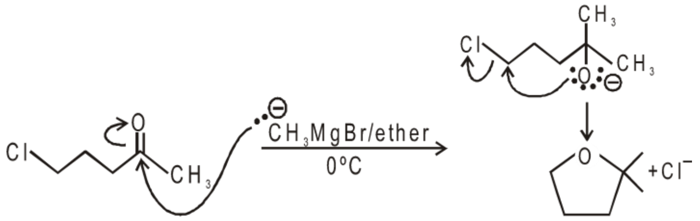
Sol.



10. **Sol.** Reaction mechanism (S_N2)

–I effect at ∝ carbon (carbon attached to leaving group) will be exerted by  hence  will be most reactive.

11. **Sol.**



ol. $Ph_3C{-}OR \xrightarrow[H_2O]{H^{\oplus}} Ph_3C{-}OH + ROH$

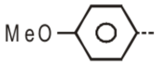
The reaction proceeds by S_N1 Mechanism :

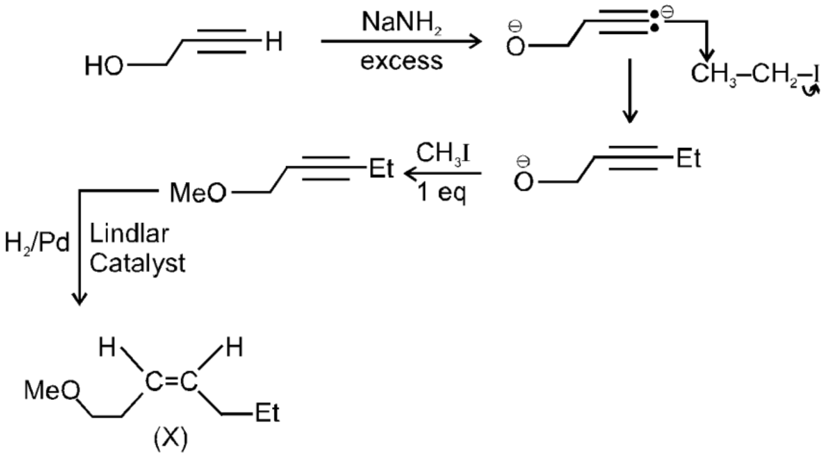
$$Ph_3C{-}OR + H^{\oplus} \rightleftharpoons Ph_3C-\overset{+}{O}HR \rightleftharpoons Ph_3C^{\oplus} + ROH$$

$$\Big\downarrow\!\!\uparrow H_2O$$

$$Ph_3C{-}OH \xleftarrow{-H^{\oplus}} Ph_3C-\overset{+}{O}H_2$$

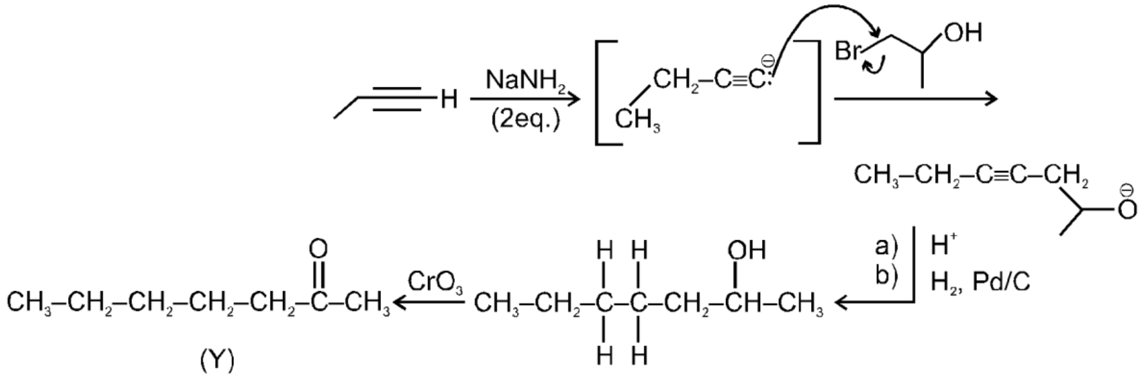
Greater the electron releasing effect of the attached groups greater is the stability of intermediate carbocation, & faster is the rate of reaction.

If two ph– groups are replaced by  groups , strong +M effect of MeO– groups stabilize, the carbocation better there by making the reaction faster.



13. **Sol.**

14. Sol.



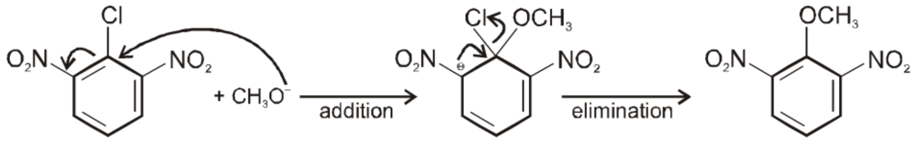
(Y) can give iodoform test (but not Tollen's test and it is a functional isomer of (X)

Additional Problems for Self Practice (APSP)

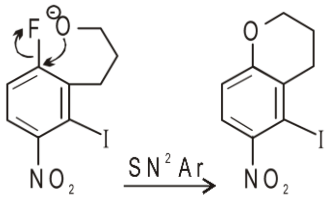
PART - I : PRACTICE TEST PAPER

1.

Sol.

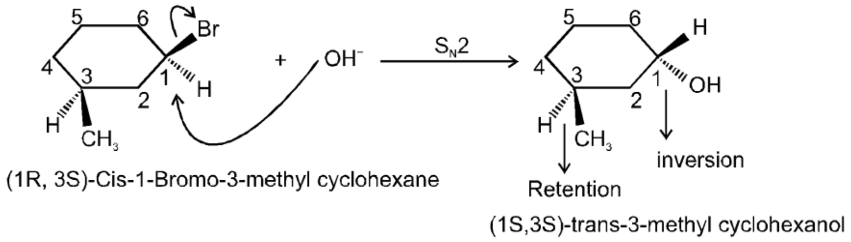


2. **Sol.**



3. **Sol.** It is a S_N2 reaction, so inversion takes place at sp^3 carbon.

5. **Sol.**

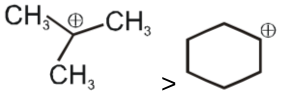


(1R, 3S)-Cis-1-Bromo-3-methyl cyclohexane

(1S,3S)-trans-3-methyl cyclohexanol

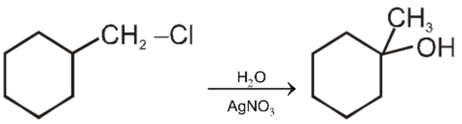
6. **Sol.** On the basis of carbocation stability.

7. **Sol.** Carbocation Stability



Leaving group ability is $Br^{\ominus} > Cl^{\ominus}$
Over all reaction order $r_1 > r_3 > r_2$

8. **Sol.**



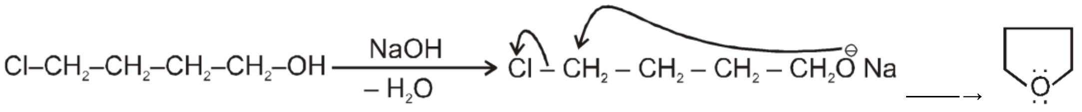
10. **Sol.** 1º R-X gives S_N2 reaction fastest and 3º R-X gives S_N1 reaction fastest.

11. **Sol.** It is a nucleophillc aromatic substitution reaction.

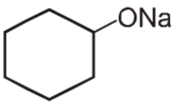
12.^ **Sol.** Strong anionic Nucleophile so mechanism is S_N2.

13. **Sol.** Polar aprotic solvent favours S_N2 mechanism.

14. **Sol.**



15. **Sol.**



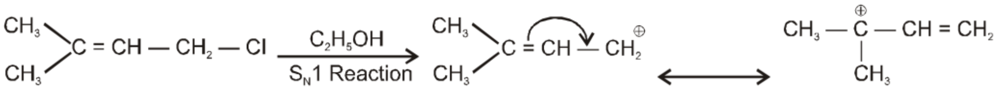
$+ CH_3I$ —→

strong anionic nucleophile and 1º alkyl halide favours S_N2 mechansim.

16. **Sol.** $-\overset{\ominus}{O}SO_2CF_3$. is better Leaving group and CH_3OH give S_N1 product as a major product.

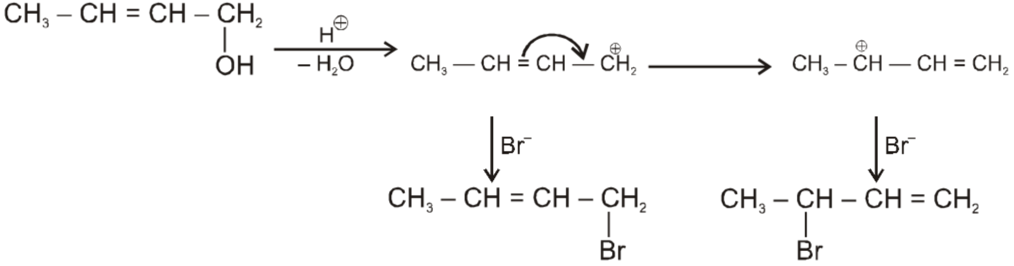
17.

Sol. (1)

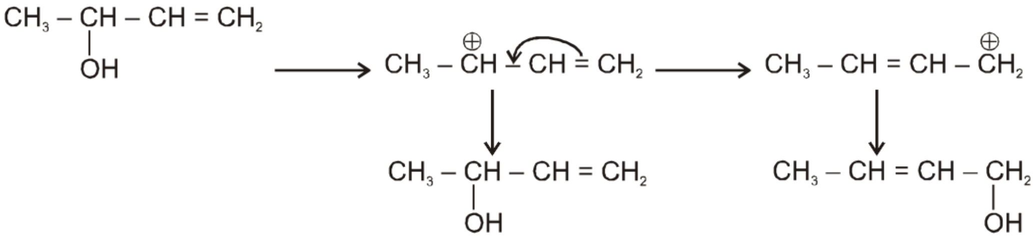


$$\underset{(1^\circ\ R–X)}{R—X} \xrightarrow{S_N} \text{No stable carbocation}$$

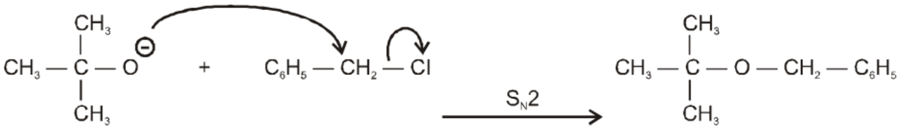
(2)



(3)

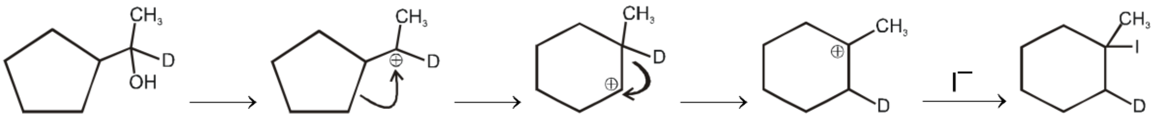


18. **Sol.**

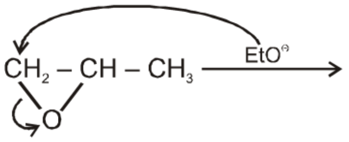


19.

Sol.



20. **Sol.**



$\mathrm{EtO{-}CH_2{-}\overset{\overset{CH}{|}}{O^{\ominus}}{-}CH_3} \xrightarrow{EtOH} \mathrm{EtO{-}CH_2{-}\overset{\overset{CH}{|}}{OH}{-}CH_3}$

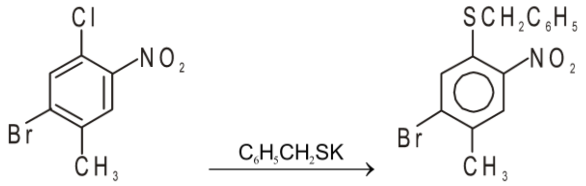
21.

Sol. Strength of Nucleophile generally increases on going down a group in the periodic table, so (4) is not true.

22. **Sol.** Nucleophilic substitution of alcohol is acid catalysed reaction.

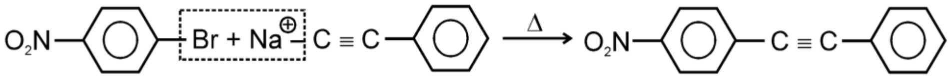
23.

Sol.



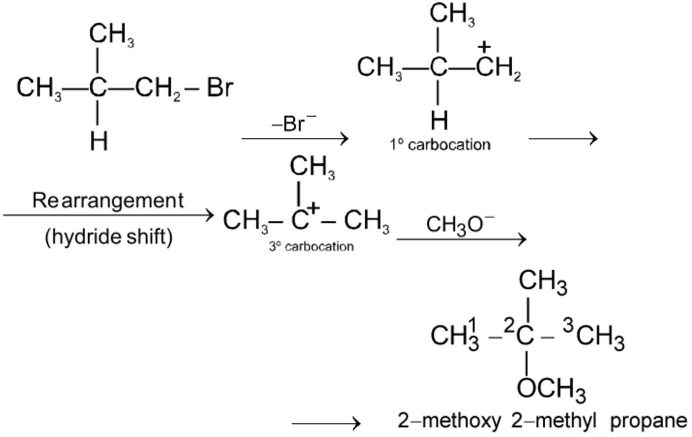
25. **Sol.** Because rate of S_N2 Ar is Ar–F > Ar–Cl > Ar–Br > Ar–I.

29. **Sol.**



PART - II : PRACTICE QUESTIONS

1. **Sol.** The reaction is an example of nucleophilic substitution reaction. The mechanism is as follows :

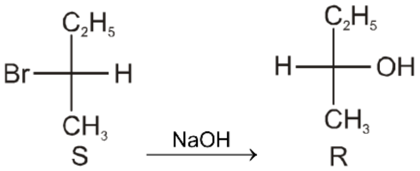


3. **Sol.** Reactivity of alkyl halides for S_N1 reaction is 3° > 2° > 1°.
So, option (4) is correct because it form more stable carbocation.

4. Sol. p-methoxy benzyl carbocation is most stable among these due to +M effect of $–OCH_3$.

5. **Sol.** 1º allyl halide gives most readily S_N2 reaction.

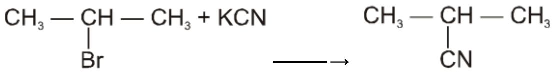
7. **Sol.** In S_N2 reaction walden inversion takes place.



9. **Sol.** $CH_3 – CH_3 \xrightarrow{Cl_2/hv} CH_3 – CH_2 –Cl \xrightarrow{KCN} CH_3 – CH_2 –CN$

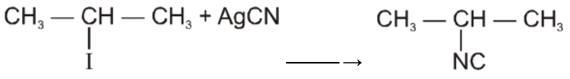
10. **Sol.** (1) $CH_3 — CH_2 — CH_2 — I + AgCN \longrightarrow CH_3 — CH_2 — CH_2 — NC$ n-propyl isocyanide.

(2)



$$\underset{\displaystyle Br}{CH_3 — \underset{|}{CH} — CH_3} + KCN \longrightarrow CH_3 — \underset{\underset{\displaystyle CN}{|}}{CH} — CH_3$$

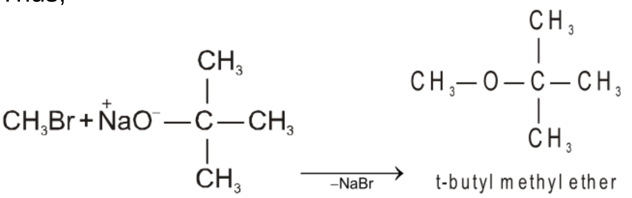
Isopropyl cyanide

(3)  Isopropyl isocyanide.

$$CH_3-\underset{I}{CH}-CH_3 + AgCN \longrightarrow CH_3-\underset{NC}{CH}-CH_3$$

(4) $(CH_3)_2\,CHCl + HCN \longrightarrow$ no. reaction.

11. **Sol.** t-butyl methyl ehter is a mixed ether and for the preparation of mixed ethers in high yield the essential condition is the use of primary alkyl halide.
Thus,



$$CH_3Br + \overset{+}{Na}O^- - C(CH_3)_3 \xrightarrow[-NaBr]{} CH_3-O-C(CH_3)_3$$

t-butyl methyl ether

(This reaction is williamson's synthesis.)

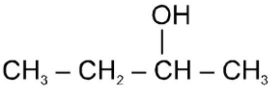
14. **Sol.** Due to electron releasing groups, decreases the rate of electrophilic substitution reaction.

17. **Sol.** $CH_3Br + AgCN \xrightarrow{\text{alcohol}} CH_3-N\equiv C$

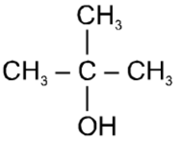
18. **Sol.**  (Most stable carbocation)

19. **Sol.** The order of reactivity with alcohols with lucas reagent is -
$3^o > 2^o > 1^o$
∴ Lucas reagent reacts fastest with 3º alcohol.

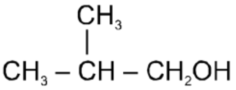
(1) $CH_3-CH_2-CH_2-CH_2OH$
butanol-1 (1° alcohol)

(2) 

$CH_3-CH_2-\overset{OH}{CH}-CH_3$
butanol-2 (2° alcohol)

(3) 

$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3$
2-methyl 2-propanol (3° alcohol)

(4) 

$CH_3-\overset{CH_3}{CH}-CH_2OH$
2-methyl 1-propanol (1° alcohol)

∴ choice (3) is the answer as it is 3º alcohol and rate of reaction is fastest for 3º alcohol.

20. **Sol.** Presence of excess of HI favours substitution reaction in ethers.
Thus the product for given reaction are $C_6H_5CH_2I$, CH_3CH_2I, $HOCH_2-CH_2OH$.